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(54) Title: USE OF ALKOXYLATED ALKANOLAMIDE AS FRICTION-REDUCING AGENT

$$\underset{\|}{\underset{O}{R\,C}}\,NH(A)_n H \qquad (I)$$

(57) Abstract

Use of an alkoxylated alkanolamide of general formula (I), wherein R is a hydrocarbon group having 7-35 carbon atoms, preferably 9-23 carbon atoms, A is an alkyleneoxy group having 2-4 carbon atoms, and n is 2-20, preferably 3-12, for producing a water-base liquid system with reduced flow resitance between the flowing, water-base liquid system and a solid surface.

USE OF ALKOXYLATED ALKANOLAMIDE AS FRICTION-REDUCING AGENT

The present invention relates to the use of an
5   alkoxylated alkanolamide in a water-base system for reduc-
ing the flow resistance between a solid surface and the
water-base liquid system.

It is well-known that the flow resistance of a liquid
in a conduit is largely due to the turbulence that arises
10   at the conduit wall. However, much of this turbulence can
be prevented by adding to the liquid a sufficient amount
of elongate particles. The size of these particles may
vary within several orders of magnitude, from severed
textile fibres, water-soluble chain molecules down to
15   cylindrical surfactant micelles, i.e. within the range of
10^{-7}-10^{-2} m. The reduction of the pressure drop that can
be achieved by such additions is considerable, and has, in
commercial hot-water systems, been assessed at 75%, which
involves corresponding savings in supplied pump energy or,
20   alternatively, permits further extension of the distribu-
tive network with the same pump installations.

In most cases, the addition of fibres is inconve-
nient, since various filters often are incorporated in
circulating liquid systems, and the water-soluble chain
25   polymers are torn by the high shear forces in the pumps
and thereby lose their effect.

Surfactants with the ability to form extremely long,
cylindrical micelles have, in recent years, attracted a
great interest as friction-reducing additives to systems
30   with circulating water, especially those destined for heat
or cold distribution.

An important reason for this interest is that,
although one desires to maintain a laminar flow in the
conduits, one wishes at the same time to have turbulence
35   in the heat exchangers to achieve therein a high heat
transfer per unit area.

2

As may easily be understood, fibres or chain polymers are unable to provide this double function which, however, can be achieved with rod-shaped micelles, since the flow rate (the Reynold's number) usually is much higher in the heat exchangers than in the conduit.

The rod-shaped micelles are distinguished by operating in a fairly disorderly fashion at low Reynold's numbers (below 10^4) and having no or only a very slight effect on the flow resistance.

At higher Reynold's numbers (above 10^4), the micelles are paralleled and result in a friction reduction very close to that which is theoretically possible.

At even higher Reynold's numbers (e.g. above 10^5), the shear forces in the liquid become so high that the micelles start to get torn and the friction-reducing effect rapidly decreases as the Reynold's numbers increase.

The range of Reynold's numbers within which the surface-active agents have a maximum friction-reducing effect is heavily dependent on the concentration, the range increasing with the concentration.

By choosing the right concentration of surface-active agents and suitable flow rates in tubings and heat exchangers, it is thus possible to establish a laminar flow in the tubes and turbulence in the heat exchangers. Thus, the dimensions of both the tubes and the exchangers can be kept at a low level, or the number of pump stations, and consequently the pump work, can alternatively be reduced while retaining the same tubular dimensions.

The surface-active agents hitherto used as friction-reducing additives to circulating water systems - mainly destined for heat or cold distribution - are all of the type alkyltrimethyl ammonium salicylate of the chemical formula

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wherein R represents a long alkyl chain which has 16-22
carbon atoms and which may either be saturated or contain
one or more double bonds.

This type of surface-active agent functions satisfac-
5   torily already at a concentration of 0.5-1 g/l, but is
degraded very slowly, both aerobically and anaerobically,
and further is highly toxic to marine organisms.

Since heat-distribution systems for small houses
usually suffer from important leaks (it is estimated that
10 in one year 60-100% of the water leaks out), it follows
that the added chemicals end up in the ground water and in
various fresh-water recipients. This combination of low
biodegradability and high toxicity is a fundamental
criterion for a product injurious to the environment.

15   Thus, there is a general demand for surface-active
agents which are less harmful to the environment but which
have the same excellent ability as the quaternary ammonium
compounds described above to reduce the flow resistance in
circulating water systems.

20   It has now surprisingly been found that a long since
well-known type of non-ionic surface-active agents, namely
alkoxylated alkanolamides, are capable of forming long
cylindrical micelles. In flow tests in water-base systems,
they had a friction-reducing effect well up to the effect
25 achieved by the above-mentioned alkyltrimethyl ammonium
salicylate. To be more specific, the invention relates to
the use of an alkoxylated alkanolamide of the general
formula
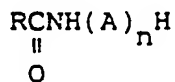
$$RC\underset{\overset{\|}{O}}{N}H(A)_nH$$

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wherein R is a hydrocarbon group having 7-35 carbon atoms,
preferably 9-23 carbon atoms, A is an alkyleneoxy group
having 2-4 carbon atoms, and n is 2-20, preferably 3-12,
35 for producing a water-base liquid system with reduced flow
resistance between the liquid water-base system and a

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solid surface. By 'water-base' is meant that at least 50%
by weight, preferably at least 90% by weight, of the
water-base liquid system consists of water. The alkoxylat-
ed alkanolamide is especially suited for use in water-base
5 systems flowing in long conduits, e.g. circulating water
systems for heat or cold distribution. The amount of
alkoxylated alkanolamide may vary within wide limits
depending on the conditions, but generally is 100-10,000
g/m^3 of the water-base system.

10   The alkoxylated alkanolamide can be produced by ami-
dation of a carboxylic acid of the formula RCOOH, wherein
R has the meaning stated above, with an alkanolamine of
the formula NHAH, wherein A has the meaning stated above,
or by aminolysis of a corresponding triglyceride or methyl
15 ester with the above-mentioned alkanolamine followed by
alkoxylation of the resulting amide. The alkoxylation may
be carried out in the presence of an alkaline catalyst at
a temperature of 150-180°C.

     It is especially suitable to carry out the alkoxyla-
20 tion in the presence of a tertiary amine lacking protons
that react with alkylene oxide, or an alkylene-oxide-
quaternised derivative of the tertiary amine at a tempe-
rature ranging from room temperature to 120°C, which
results in high yields of the desired product. Suitable
25 tertiary amines include trimethylamine, triethylamine,
tributylamine, dimethyloctylamine, tetramethylethylene-
diamine, dimethyl coconut amine, tristearyl amine,
dimethyl piperazine and diazabicyclooctane.

     The alkoxylation may comprise ethoxylation, propoxy-
30 lation, addition of propylene oxide and ethylene oxide in
blocks, simultaneous addition of ethylene oxide and pro-
pylene oxide, or a combination thereof. The ethylene oxide
conveniently amounts to at least 50 mole% of the added
alkylene oxide. To use only ethoxylation is preferred.

35   The carboxylic acids of the formula RCOOH, wherein R
has the meaning stated above, may be aliphatic, aromatic
as well as cyclo-aliphatic. Suitable carboxylic acids

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include the aliphatic carboxylic acids in which the hydro-
carbon part may be saturated or unsaturated, straight or
branched. To use conventional fatty acids is especially
preferred.

5   Suitable alkoxylated alkanolamides include the fol-
lowing specific examples:

$$RC\overset{\overset{O}{\|}}{N}H(C_2H_4O)_4\overset{\overset{O}{\|}}{H}, \text{ wherein RC is derived from rape oil}$$
fatty acid,

10
$$RC\overset{\overset{O}{\|}}{N}H(C_2H_4O)_7\overset{\overset{O}{\|}}{H}, \text{ wherein RC is derived from rape oil}$$
fatty acid,

$$RC\overset{\overset{O}{\|}}{N}HC_3H_6O(C_2H_4O)_3\overset{\overset{O}{\|}}{H}, \text{ wherein RC is derived from lauric}$$
15 acid,

$$RC\overset{\overset{O}{\|}}{N}H(C_2H_4O)_4\overset{\overset{O}{\|}}{H}, \text{ wherein RC is derived from lauric acid,}$$

$$RC\overset{\overset{O}{\|}}{N}HC_2H_4O(A)_4\overset{\overset{O}{\|}}{H}, \text{ wherein RC is derived from stearic}$$
20 acid, and

the group A is random added from equal mole parts of ethy-
lene oxide and propylene oxide

25
$$RC\overset{\overset{O}{\|}}{N}HC_4H_8O(C_2H_4O)_{10}\overset{\overset{O}{\|}}{H}, \text{ wherein RC is derived from lino-}$$
lenic acid.

The choice of chain length and degree of unsaturation
is determined by the temperature range in which the
30 alkoxylated alkanolamide is to operate. A higher tempera-
ture requires a larger hydrocarbon group and less unsatu-
ration. The choice of the degree of alkoxylation is
determined by the size and degree of saturation of the
hydrocarbon group as well as by the temperature. Whether
35 the right degree of alkoxylation has been reached is
easily established by determining the cloud point of the

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alkoxylated alkanolamide in a 1% solution in the water-base system. Below the cloud point, i.e. the alkoxylated alkanolamide is solved in the water-base system, the ability of the alkoxylated alkanolamide to reduce the flow

5 resistance increases as the temperature increases, whereas this ability decreases at higher temperatures, at which the alkoxylated alkanolamide is precipitated. Thus, the degree of alkoxylation and the alkyleneoxy group present should be selected in such a manner that the cloud point

10 of the alkoxylated alkanolamide is equal to or slightly below the temperature prevailing in the water-base system at laminar flow, e.g. at Reynold's numbers between 10^4 and 10^5. When the temperature of the water-base system varies considerably, e.g. when the system is used as heating

15 medium in long tubings, the cloud point of the alkoxylated alkanolamide should at least exceed the lowest temperature prevailing in the water-base system at laminar flow. Preferably, the cloud point should exceed the highest temperature of the water-base system at laminar flow. Adjust-

20 ment to the desired cloud point may conveniently be performed by mixing alkoxylated alkanolamides of different cloud points. Such mixtures may also be advantageous when the temperature in the water system at laminar flow varies considerably.

25　　When using the water-base system for cold distribution, it is essential that the Krafft point of the alkoxylated alkanolamide, i.e. the temperature at which the alkoxylated alkanolamide starts to crystallise in the water-base system, is below the lowest temperature in the

30 water-base system. The Krafft point may be decreased by selecting fatty acids with shorter alkyl chains and/or unsaturated fatty acids. A higher degree of ethylation as well as incorporation of soluble salts in the water-base system will also decrease the Krafft point. When used as a

35 cooling medium, the temperature of the water-base system is suitably below 30°C, preferably below 20°C.

　　Apart from the alkoxylated alkanolamide, the water-

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base system may contain a number of conventional compo-
nents, such as rust-preventing agents, anti-freeze, and
bactericides. The system may also include solubilisers,
such as diethylene glycol monobutyl ethers, which may
5   affect the cloud point of the alkoxylated alkanolamides in
the water-base system quite considerably.

The present invention will now be further illustrated
with the aid of the following Example.

Exemple

10   Measurements were carried out in a 6-m tube loop
consisting of two straight and stainless tubes (3 m each),
one tube having an inner diameter of 8 mm and the other
having an inner diameter of 10 mm. Water was pumped
through the tube loop by a centrifugal pump, which was
15   driven by a frequency-controlled motor, for continuous
adjustment of the flow rate, which was determined by a
rotameter.

The straight parts of the tube loop had outlets
which, with the aid of valves, could in turn be connected
20   to a differential pressure gauge whose other side was all
the time connected to a reference point in the tube loop.
Further, the tube loop was heat-insulated, and the suction
side of the pump was connected to a thermostatically
controlled container with a volume of 20 l, to which the
25   return flow from the tube loop was directed.

After the testing compound had been added and the
aqueous solution had been thermostatically controlled,
measurements began at low flow rates, and the pressure
difference from two points on the 10-mm tube and three
30   points on the 8-mm tube were measured for each flow rate.
The pressure differences thus measured were then converted
into Moody's friction factor Y and are shown in the Table
below as a function of the Reynold's number Re.

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$$Y = 2D.P_{diff}/V^2.L.d$$

Re = D.V.d/u

D = tube diameter

V = flow rates

L = tube length over which the pressure difference P_{diff} was measured

d = density of the liquid

u = viscosity of the liquid

The Table also states the corresponding Prandtl number and Virk number. The former corresponds to the friction factor of water only, i.e. with turbulence, and the latter corresponds to flow without turbulence.

One of the following compounds was added as testing compound   A   Cetyl trimethyl ammonium salicylate

B C_{12-14} alcohol + 6 EO

C   50% by weight of rape oil fatty acid ethanolamide + 3 EO

50% by weight of rape oil fatty acid ethanolamide + 6 EO

(The cloud point of the mixture was 56°C in water)

The following results were obtained.

Table 1

Compound A, addition of 1000 ppm, temperature of 50°C

Reynold's number	Moody's friction fractor . 10^3				
	10^4	2×10^4	4×10^4	6×10^4	8×10^4
Prandtl number	30	24	22	21	20
10 mm	35	15	8.0	6.0	17
8 mm	30	12	6.0	6.0	18
Virk number	10	8	5.5	4.5	3.0

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Table 2

Compound B, addition of 20 g/l, temperature of 80°C,
Moody's friction factor

Reynold's number	Moody's friction factor . 10^3				
	10^4	2×10^4	4×10^4	6×10^4	8×10^4
Prandtl number	30	24	22	21	20
10 mm	-	14	14	13	13
8 mm	-	12	15	14	14
Virk number	10	8.0	5.5	4.5	3.0

Table 3

Compound C, addition of 6000 ppm, temperature of 25°C,
Moody's friction factor

Reynold's number	Moody's friction factor . 10^3				
	10^4	2×10^4	4×10^4	6×10^4	8×10^4
Prandtl number	30	24	22	21	20
10 mm	15	9	6.0	5.0	10
8 mm	20	10	6.5	11	15
Virk number	10	8.0	5.5	4.5	3

   As is apparent from these results, the invention
gives a friction reduction down to the theoretically pos-
sible level (the Virk line), in analogy with prior-art
results with alkyltrimethyl ammonium salicylate, and this
is not possible with common non-ionic surface-active
agents of the type fatty alcohol ethoxylate. Compared with
the prior-art quaternary ammonium compounds, the friction-
reducing agent according to the invention is advantageous
in that it is much less toxic to water organisms and is
biologically degraded much faster, both aerobically and
anaerobically. The friction-reducing agent according to
the invention may thus be used as a friction-reducing
additive also to heat-distribution systems where there is
a certain amount of leakage.

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CLAIMS

1. Use of an alkoxylated alkanolamide of the general formula
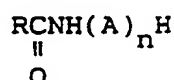
$$RCNH(A)_nH$$
$$\underset{O}{\overset{\parallel}{}}$$

wherein R is a hydrocarbon group having 7-35 carbon atoms, preferably 9-23 carbon atoms, A is an alkyleneoxy group having 2-4 carbon atoms, and n is 2-20, preferably 3-12, for producing a water-base liquid system with reduced flow resistance between the flowing, water-base liquid system and a solid surface.

2. Use as claimed in claim 1, c h a r a c t e r - i s e d in that n is so chosen that the alkoxylated alkanolamide, in the concentration in which it is used in the water-base system, has a cloud point which is higher than the lowest temperature of the water-base system at laminar flow.

3. Use as claimed in claim 2, c h a r a c t e r - i s e d in that the cloud point is higher than the highest temperature of the water-base system.

4. Use as claimed in claim 1, 2 or 3, c h a r a c - t e r i s e d in that the water-base system is a hot-water system with a temperature exceeding 60°C.

5. Use as claimed in claim 1, 2 or 3, c h a r a c - t e r i s e d in that the water-base system is a cooling medium with a temperature below 30°C.

6. Use as claimed in any one of claims 1-5, c h a r - a c t e r i s e d in that the alkoxylated alkanolamide is added in an amount of 100-10,000 g/cm^3 of the water-base system.

7. Use as claimed in any one of claims 1-6, c h a r - a c t e r i s e d in that at least half of the alkyleneoxy groups are ethyleneoxy groups.

8. Use as claimed in claim 7, c h a r a c t e r i s -
e d   in that A is an ethyleneoxy group.

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I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]
According to International Patent Classification (IPC) or to both National Classification and IPC
IPC5: C 09 K 3/00, C 07 C 233/17, F 15 D 1/02, C 10 M 105/04

II. FIELDS SEARCHED

Minimum Documentation Searched[7]	
Classification System	Classification Symbols
IPC5	C 07 C; C 09 K; C 10 M; F 15 D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]
SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category*	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	EP, A1, 0147489 (MOBIL OIL CORPORATION) 10 July 1985, see page 1, line 1 - line 15; claim 1	1-8
A	EP, A2, 0146097 (HOECHST AKTIENGESELLSCHAFT) 26 June 1985, see page 1, line 1 - line 3; claim 1	1-8
A	SE, B, 425849 (L'OREAL) 15 November 1982, see page 6 - page 7; claim 1	1-8
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* Special categories of cited documents: [10]

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
28th April 1992	1992 -05- 0 6
International Searching Authority	Signature of Authorized Officer
SWEDISH PATENT OFFICE	Bengt Christensson

III. DOCUMENTS CONSIDERED TO BE RELEVANT   (CONTINUED FROM THE SECOND SHEET)

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A	SE, B, 363092 (ROHM AND HAAS COMPANY) 7 January 1974, see claim 1 --	1-8
A	GB, A, 1145740 (DISTILLERS CHEMICALS AND PLASTICS LIMITED) 19 March 1969, see column 1, line 13; claim 1 --	1-8

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